

Chapter 6

The Nitrogen Chemistry in Hot Jupiters Atmosphere

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Abstract The atmosphere of hot Jupiters can be probed by primary transit and secondary eclipse spectroscopy. In order to constrain the atmospheric thermal structure and composition from observables, chemical models are necessary. Due to the intense UV irradiation, mixing and circulation, the chemical composition is maintained out of equilibrium and kinetic photochemical models must be applied with kinetics valid at the high temperatures prevailing in hot Jupiters atmospheres. We study the steady state atmospheric composition of HD 189733b one of the most observed hot Jupiters by implementing a new kinetic network in a 1D time-dependent chemical model including photodissociations and vertical diffusion. We confirm that the atmospheric composition of the planet is maintained out of the equilibrium by photodissociations and vertical quenching. The core and novelty of this study is the chemical scheme. It was produced in close collaboration with experts of applied high-temperature kinetics and methodically validated over a range of temperatures and pressures typical of the atmospheric layers influencing the observations of hot Jupiters. In addition to our nominal chemical scheme, we implemented other reaction sub-networks for nitrogen-bearing species that are

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commonly used in the field of combustion, and investigate the sensitivity of the predicted abundances and spectra to the network. We found that the abundances of NH_3 and HCN can vary by 2 orders of magnitude. A spectral feature of NH_3 at $10.5\ \mu\text{m}$ is sensitive to these abundance variations and thus to the chemical scheme.

Introduction

So far, more than 700 exoplanets have been confirmed and thousands of transiting candidates have been identified by the space telescope Kepler [4]. Among them, hot Jupiters are a class of gas giants with orbital periods of a few days or less. They are found around $\sim 0.5\%$ of KGF stars [29, 30]. About 10% of them transit their host star and their atmospheric composition and physical structure can be studied by transit spectroscopy [12, 13, 31, 52, 58, 62–66]. Photochemical models have been developed to interpret these observations [44–46, 50, 73].

Because of their short orbital distance, hot Jupiters receive a high UV flux (typically 10,000 times the flux received on the top of the atmosphere of Jupiter) and their equilibrium temperature is very high (ranging from 600 to 3,000 K). Thus, the atmospheric composition of these planets is potentially influenced by both photochemistry and thermochemistry [73].

In Solar System atmospheres, photolyses due to solar UV photon occur at low temperature and chemical models can neglect endothermic reactions. In the hot lower atmospheres of gas giants, icy giants, and Venus, temperature is high enough for endothermic reactions to take place but no UV radiation is present. Therefore, we cannot use the same models to describe correctly hot Jupiter atmospheres, since it is necessary to consider chemical reactions in both the exothermic and endothermic directions, with rate coefficients specific to the relevant temperature range, as well as UV photolyses. To that purpose, we have implemented a chemical scheme that is new in the field of astrochemistry, but initially developed for industrial applications (mainly combustion in car engines). Chemical models based on this scheme have been the subject of a comprehensive validation against experiments.

Chemical Modeling

Kinetics and Thermodynamic Equilibrium

An elementary reversible reaction i involving J chemical species can be represented in the following general form:

$$\sum_{j=1}^J \nu'_{ji} \chi_j \rightleftharpoons \sum_{j=1}^J \nu''_{ji} \chi_j \quad (6.1)$$

where v'_{ji} are the forward stoichiometric coefficients, and v''_{ji} are the reverse ones. χ_j is the chemical symbol of the j th species. The kinetic data associated to each reaction are expressed with a modified Arrhenius law $k(T) = A \times T^n \exp^{-\frac{E_a}{RT}}$ where T is the temperature, R the universal gas constant, E_a is the activation energy of the reaction, A the pre-exponential factor and n a coefficient which allows the temperature dependence of the pre-exponential factor. If the rate constant associated to the forward reaction is $k_{fi}(T)$, then the one associated to the reverse reaction is $k_{ri}(T)$, verifying:

$$K_i = \frac{k_{fi}(T)}{k_{ri}(T)} \left(\frac{P^0}{k_B T} \right)^{\sum_{j=1}^J v_{ji}} \quad (6.2)$$

where K_i is the equilibrium constant (with the activity of the reactants expressed in pressure units) [7]:

$$K_i = \exp \left(\frac{\Delta S_i^0}{R} - \frac{\Delta H_i^0}{RT} \right) \quad (6.3)$$

where ΔS_i^0 and ΔH_i^0 are the variation of entropy and enthalpy occurring when passing from reactants to products in the reaction i , P^0 is the standard pressure ($P^0 = 1,01325$ bar), k_B is the Boltzmann's constant and v_j are the stoichiometric coefficients of the J species involved in reaction i : $v_j = v''_{ji} - v'_{ji}$. The enthalpy and the entropy are expressed in therms of NASA polynomials as described in Venot et al. [71]. By reversing all the reactions, the kinetic system will evolved towards the thermodynamic equilibrium.

The equilibrium composition of a system at a defined temperature and pressure can also be determined by finding the composition that minimizes the Gibbs energy of the system. Indeed, a system always evolves in order to reduce its Gibbs energy. This energy is given by:

$$G = \sum_{j=1}^J \bar{g}_j N_j \quad (6.4)$$

where J is the total number of species, \bar{g}_j is the partial free energy of the species j and N_j is the number of moles of the species j . The partial free energy of a compound j , behaving as an ideal gas, is given by:

$$\bar{g}_j = g_j(T, P) + RT \ln N_j \quad (6.5)$$

where $g_j(T, P)$ is the free energy of the species j at the temperature T and the pressure P of the system and R is the ideal gas constant. For an ideal gas, $g_j(T, P)$ is given by:

$$g_j(T, P) = h_j^0(T) - T s_j^0(T) + RT \ln \left(\frac{P}{P^0} \right) \quad (6.6)$$

where $h_j^0(T)$ and $s_j^0(T)$ are respectively, the standard-state enthalpy and entropy of the species j at the temperature T of the system. As we said, these quantities are calculated with the NASA coefficients. Using only these coefficients, one can determine the equilibrium composition of a system.

Kinetic Network: From Car Engine to Hot Jupiters

Significant progress has been done during the past decade in the development of combustion mechanisms.¹ In the context of limiting the environmental impact of transportation, there is indeed a need in the development of detailed chemical kinetic models more predictive and more accurate for the combustion of fuels. One part of the studies undertaken in the LRGP (Laboratoire Réactions et Génie des Procédés, Nancy, France) concerns engine-fuel adaptation in order to improve the efficiency of engines and to limit the emission of pollutants. Most of these kinetic models were developed for industrial applications and have been validated in a range of temperatures, from 300 to approximately 2,500 K, and for pressures from 0.01 bar to some hundreds of bar. What is worth noticing is the similarity of these temperature and pressure ranges with the conditions prevailing in hot Jupiters atmospheres, in the very layers where they influence the observed molecular features. In addition, combustion mechanisms mainly deal with molecules made of C, H, O and N, which are also the main constituents of the molecules and radicals in these atmospheres. For this reason, we have decided to implement such a mechanism, which has already been applied successfully to many cases and systematically validated [8], to study the atmosphere of hot Jupiters.

We have used a C/H/O/N mechanism, whose core is a C₀–C₂ mechanism that includes all the reactions required to model the kinetic evolution of radicals and molecules containing less than three carbon atoms. This mechanism is described in Venot et al. [71]. The originality of this scheme, is that it includes experimental data for both exothermic and endothermic directions for three important reactions, instead of reversing them with the equilibrium constant. Indeed, we have explained in section “Kinetics and Thermodynamic Equilibrium” that it was necessary to reverse all the reactions of a system to reproduce the thermodynamical equilibrium, but it does not ensure that the kinetic evolution is realistic. Decade of study and experiments in the field of combustion have shown that the kinetic evolution was more realistic using experimental data for some reactions for both directions.

As nitrogen species, such as N₂, NH₃, HCN, are expected to be important constituents of hot Jupiter atmospheres, we completed this C₀–C₂ base with a validated sub-mechanism specifically constructed to model nitrogen species and all the cross-term reactions involved (for instance, reactions between alkanes and NO_x). These mechanisms do not use rate coefficients that have been adjusted by optimization procedures in order to fit experiments. Their values are those recommended for the individual processes by the main kinetics databases for combustion [6, 49, 59, 67]. The list of the reactions and their rate coefficients are

¹In the field of combustion, a *mechanism* or reaction base is a network of reactions able to describe the kinetic evolution of a given pool of species. The mechanism includes the list of reactions and the associated rate coefficients, in a modified Arrhenius form, as well as the thermodynamic data for all the species involved in these reactions, which are required to calculate the equilibrium constants of the reactions and the rates of the reverse reactions.

available in the online database KIDA: KInetic Database for Astrochemistry² [72]. The final mechanism includes 957 reversible and 6 irreversible reactions, involving 105 neutral species (molecule or radical). Helium is also included in this mechanism and plays the role of third body in some reactions.

Nitrogen Reaction Base

In our nominal model, the sub-network for the nitrogen bearing species is derived from Konnov [35, 36] and Coppens et al. [14]. It is based on a comprehensive analysis of the combustion chemistry of nitrogen oxides [38], ammonia [40], hydrazine [42], and modeling of nitrogen oxides formation in different combustion systems [37, 39, 41]. In addition, we consider a few additional pathways for HCN oxidation from Dagaut et al. [15].

Validations of our nominal sub-network for nitrogen bearing species have been made on the basis of experimental data obtained, for instance, by oxidation of HCN in a silica jet-stirred reactor (JSR) at atmospheric pressure and from 1,000 to 1,400 K [15], or studying laminar flame speeds in $\text{NH}_3 - \text{N}_2\text{O}$ mixtures [9]. The nitrogen mechanism includes 42 species: NO_3 , HONO_2 , CH_3ONO , CH_3NO_2 , HNO_2 , CH_3NO , NO_2 , HONO , HCNN , HCNO , N_2O , NCO , HNO , HOCN , NNH , H_2CN , $\text{N}(^4\text{S})$, CN , HNCO , NO , NH , NH_2 , HCN , NH_3 , N_2 , N_2O_4 , N_2O_3 , N_2H_2 , N_2H_3 , N_2H_4 , HNNO , HNOH , HNO_3 , NH_2OH , H_2NO , CNN , H_2CNO , C_2N_2 , HCNH , HNC , HON and NCN . For comparison, we have also used other nitrogen sub-mechanisms, which are presented in section “Nitrogen Reaction Base” with the corresponding results.

Because the mechanism we use was created from individual processes and validated without any optimization of their reaction coefficients, its application outside the condition range of validation is not problematic. This is an issue, for instance, with the well-known combustion mechanism GRI-Mech V3.0³ [59], proposed by Gas Research Institute, which is an optimized mechanism designed to model natural gas combustion. Optimization makes the model extremely accurate within the optimization domain but its application beyond is risky [5].

Photochemistry

We add to the thermochemical scheme a set of 34 photodissociations. In hot Jupiters, UV flux penetrates down to a pressure of about 1 bar, where the temperature is higher than 1,500 K. At these temperatures and pressures, endothermic reactions do matter, which implies that photochemistry and thermochemistry are coupled

²<http://kida.obs.u-bordeaux1.fr>.

³http://www.me.berkeley.edu/gri_mech/.

in such highly irradiated atmospheres. We used absorption cross section at the highest available temperature (i.e. 370 K at maximum, which is low compared to the temperatures in the atmosphere of hot Jupiters (see Fig. 6.1)). To tackle this issue, we have decided to measure absorption cross section at high temperature for important molecules such as CO_2 and H_2O . These measurements and their impact on the results given by our model are presented in Venot et al. [70].

Photodissociations produce excited states of oxygen ($\text{O}(^1\text{D})$) and nitrogen ($\text{N}(^2\text{D})$) that are not treated in the original combustion mechanisms. Therefore, we added to the C/H/O/N mechanism, 19 reversible reactions which describe the kinetics of $\text{O}(^1\text{D})$ and $\text{N}(^2\text{D})$, including radiative and collisional desexcitation. These reactions rates are taken (or have been estimated) from Okabe [51], Herron [28], Umemoto et al. [69], Balucani et al. [2], Sato et al. [55], Balucani et al. [3] and Sander et al. [54].

1D Numerical Model

We use this chemical network in a 1D model that includes photolyses and vertical transport, which has been previously used to study the atmospheric photochemistry of various objects of the Solar System: Neptune [19], Titan [26, 27], Saturn [11, 18], and Jupiter [10] as well as extrasolar terrestrial planets [56]. This model has been adapted to hot Jupiters and is described in Dobrijevic et al. [19] and Venot et al. [71].

To calculate the photodissociation rates in all the layers of the atmosphere, we compute the stellar UV flux as a function of pressure and wavelength, taking into account molecular absorption by 22 species and Rayleigh scattering. Actinic fluxes are calculated with a resolution of 1 nm (which is also the resolution we adopted for the absorption cross-sections), assuming a plane parallel geometry and an incidence angle θ of 48° (because $\langle \cos \theta \rangle = 2/3$ ($\theta \simeq 48^\circ$) is the projected-areaweighted average of the cosine of the stellar zenith angle over the planetary disk at secondary-eclipse conditions). Multiple Rayleigh scattering is coupled with absorption through a simple two-stream iterative algorithm [34].

Application to HD 189733b

HD 189733b transits around a nearby bright star. Its atmosphere has been studied by the transmission spectrum obtained during the primary transit and the day-side emission spectrum measured at the secondary eclipse. These observations can be used to constrain the thermal profile [47] and to detect the spectral signature of atmospheric compounds [24, 63, 65, 66].

The physical properties used for HD 189733b and HD 189733 come from Southworth [60, 61]. We use the temperature (Fig. 6.1) and eddy diffusion profiles published in Moses et al. [50]. These profiles are derived from the general

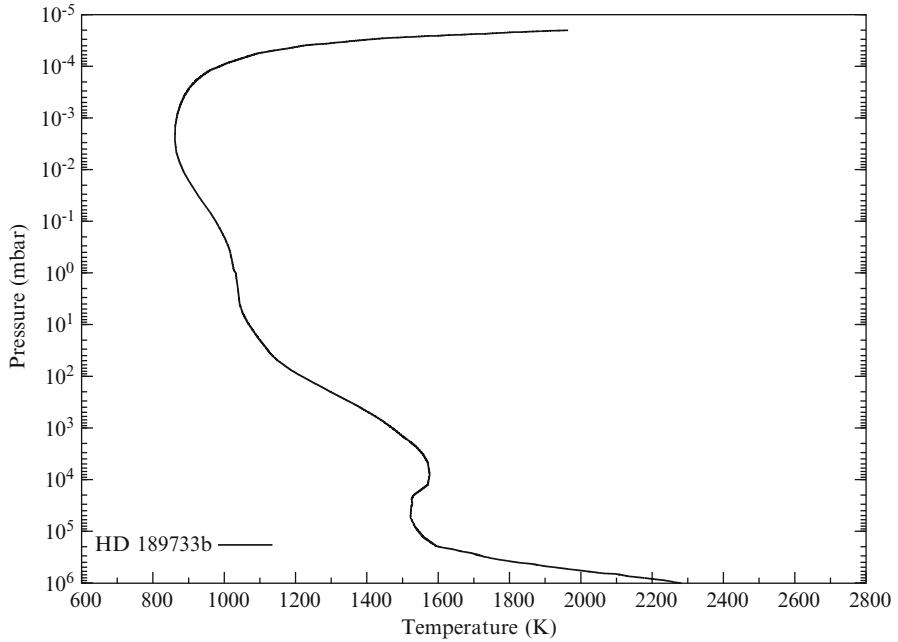


Fig. 6.1 Pressure-temperature profiles of HD 189733b (From [50])

circulation model of Showman et al. [57] (for $K(z)$ and PT profiles) and the 1-D model of Fortney et al. [21, 22] (for PT profile only). Also following Moses et al. [50], we assume solar elemental abundances for this planet, with 20 % of depletion for oxygen (sequestered along with silicates and metals). We start our time-dependent modeling with the thermodynamic equilibrium abundances calculated with TECA (an equilibrium model described in Venot et al. [71]) at each level of the atmosphere.

For the star HD 189733, a K1–K2 star, the UV spectrum has been provided to us by Ignasi Ribas (private communication). It is based on FUSE and HST observations of the star ϵ Eridani, a proxy of HD 189733 (similar type, age and metallicity), in the 90–330 nm range and on scaling laws between 0.5 and 90 nm. Above 330 nm, we use a synthetic spectrum calculated with the stellar atmosphere code Phoenix [25].

Nominal Model

First of all, we checked that our kinetic model reproduces the thermodynamic equilibrium, in the absence of vertical mixing and photodissociation. We obtained differences lower than a few percent. The homopause is found above the 1×10^{-5} mbar level, which is beyond the range of pressure that we model. As a consequence, and although it is included, molecular diffusion does not affect our results.

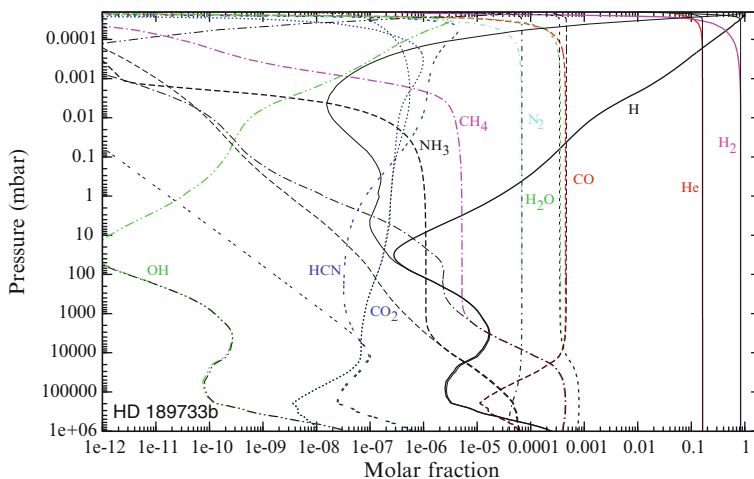


Fig. 6.2 Steady-state composition of HD 189733b calculated with our nominal model (*color lines*), compared to the thermodynamic equilibrium (*thin black lines*)

Figure 6.2 shows the steady-state composition of the atmosphere of HD 189733b, with vertical transport and photodissociations. The vertical quenching has an effect on a large part of the atmosphere of HD 189733b. NH_3 and HCN are quenched at 5 bar, CH_4 at 1 bar, H at 40 mbar and CO_2 at 20 mbar. Quenching contaminates the composition up to very low-pressure levels (10^{-4} mbar).

Photodissociations affect the composition down to about the 10 mbar level. The production of H is dominated by the photolysis of H_2 for pressures lower than 1 μbar . Below this level, and for pressures higher than 0.1 mbar, H is produced by the photodissociation of H_2O , with a minor contribution of the photodissociations of NH_3 and HCN . The abundance of OH follows the profile of H , and increases for pressures lower than 10 mbar. There is a photochemical enhancement of HCN above the 10 mbar pressure level, as discussed in Moses et al. [50]. CH_4 is destroyed by photolyses for pressures lower than 0.01 mbar. NH_3 is photodissociated down to levels as deep as 1 bar, but vertical transport compensates this destruction for pressures higher than 0.1 mbar. Above that level, the amount of NH_3 decreases with altitude due to photolyses. Photochemistry has a negligible effect on CO_2 , as noted by Zahnle et al. [73].

Other Networks for Nitrogen Species

The chemistry of some nitrogen compounds is not well constrained. However, NO_x , HCN , CN and NH_3 are important species in applied combustion (gas fuel, for instance, can contain high concentrations of ammonia), and should be well

reproduced within the temperature and pressure range of the validation. Quenching is found to occur within 100 to a few hundred bars, a pressure range at which our nominal mechanism has been validated. Other sub-mechanisms are available to model the kinetics of nitrogen-bearing species. In order to test how our results are sensitive to the nitrogen scheme, we replaced our nitrogen reaction base by other nitrogen sub-mechanisms:

- *GRIMECH*, mechanism based on GRI-Mech 3.0 [59] with several reactions involving NO_x compounds added with respect to the mechanisms of Glaude et al. [23] as recommended and done by Anderlohr et al. [1]. It includes 162 reversible reactions involving 26 nitrogen compounds. The GRI-Mech 3.0 is a mechanism designed to model natural gas combustion, including NO formation and reburn chemistry. As already mentioned in section “Nitrogen Reaction Base”, it has been optimized as a global mechanism, i.e., some rate coefficients have been modified (compared to the literature) in order to fit the results of a pool of experiments with conditions and compositions specific to combustion. The individual processes have not been studied separately in all the pressure and temperature range. Applying this mechanism beyond its domain of optimization/validation is a risky extrapolation. Mixing ratios of oxidants, for instance, are very low in hot Jupiter atmospheres compared with the experiments used to optimize/validate GRI-Mech 3.0.
- *GDF-Kin*, mechanism for natural gas combustion modeling [16, 68] that includes 180 reversibles reactions involving 22 nitrogen species. Several experimental data on natural gas combustion have been acquired in partnership with *Gaz de France* to develop and optimize this mechanism. NO_x chemistry has been included in GDF-Kin 3.0 [20]. We use the update version GDF-Kin 5.0 [43], in which five reactions involving NCN have been refined in order to better reproduce the kinetics of this species.
- *DEAN*, taken from Dean and Bozzelli [17]. This book that presents a catalog of reactions is used by Moses et al. [50], at least for some reactions. The mechanism derived from this work includes 370 reversible reactions involving 49 nitrogen species and one C/H/O species that is not included in our $\text{C}_0\text{--C}_2$ scheme: HCOH. The purpose of the work of Dean and Bozzelli was to list gas phase reactions involving nitrogen-bearing species that could be important for high temperature combustion modeling and to provide the associated rate coefficients based on an analysis of elementary reaction data, when available, or on estimations from thermochemical kinetics principles otherwise. This mechanism was developed on the basis of analysis of individual reactions rather than by attempting to reproduce any specific set of experiments. It is clearly written in this book that: “Although we show in the chapter that this mechanism provides a reasonable description of some aspects of high-temperature nitrogen chemistry, we have not attempted a comprehensive comparison”. Therefore, this kinetic network should be viewed as a database of reaction rate constants rather than a real validated mechanism.

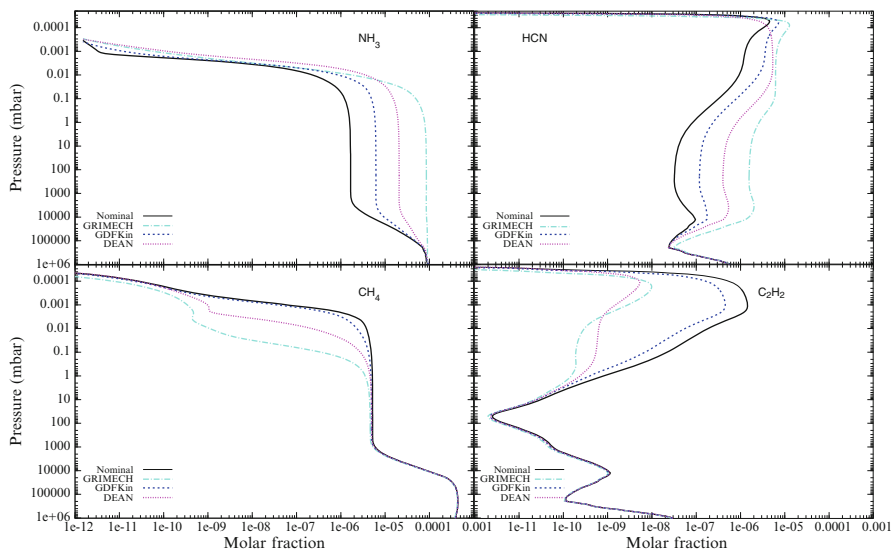


Fig. 6.3 Abundances of NH_3 , HCN , CH_4 and C_2H_2 in HD 189733b with the four different models

The impact of the different nitrogen sub-mechanisms on the abundance profiles of various species is illustrated in Fig. 6.3. Thermodynamic equilibrium is the same for all schemes (for the species in common).

The main species that are significantly affected at these pressure levels by the change of nitrogen scheme are HCN and NH_3 . This is not surprising as these are the only ones departing from equilibrium due to quenching, and the pressure level at which the quenching occurs depends on the kinetic network adopted. For both HCN and NH_3 , profiles obtained with *GDF-Kin* are bracketed by those from the nominal model and *DEAN*, while *GRIMECH* gives significantly higher abundances than all other models in the quenching region. With *GRIMECH*, we also notice that NH_3 becomes the main nitrogen-bearing species from the bottom of the atmosphere up to 0.03 mbar because of vertical mixing, whereas thermodynamics predicts that N_2 should be the main nitrogen-bearing species.

For hydrocarbons (see Fig. 6.3) all the models we tested cluster to the same profiles for pressures below 1 mbar. This shows that N-bearing species have little influence on hydrocarbon chemistry at these altitudes (This would no longer be true at higher temperature and for higher C/O ratios as HCN would become a major reservoir of both N and C).

At lower pressure, Fig. 6.3 shows large differences that are no longer due to quenching. When comparing our nominal model with our alternative ones, departures can be due to differences in the kinetic network (different rates, different minor species included) and in photochemistry, as some absorbing species are not included in all the models. The difference is particularly striking for C_2H_2 , where

DEAN and *GRIMECH*, on the one hand, and the nominal model and *GDF-Kin*, on the other hand, seem to cluster in two different regimes, exhibiting 2 to 3 order of magnitude differences at 0.1–0.001 mbar.

Corresponding Emission and Transmission Spectra

In order to calculate the planetary transmission and emission+reflection spectra of HD 189733b (Fig. 6.4), we use a line-by-line radiative transfer model from 0.3 to 25 μm [32, 33]. The opacity sources included in the model are the main molecular constituents: H_2O , CO , CH_4 , NH_3 , Na , K and TiO ; Collision Induced Absorption by H_2 and He ; Rayleigh diffusion and H^- bound-free and H_2^- free-free. For absorbing species not included in our kinetic model (Na , K and TiO), chemical equilibrium is assumed. The current model does not account for clouds. For the reflected component, we use synthetic stellar spectra generated from ATLAS.⁴ The main difference from the static model described in Iro et al. [33] is the addition of NH_3 for which we used the HITRAN 2008 database [53].

We applied this model for the compositions obtained with the two nitrogen mechanisms, which give the most opposite results (Nominal and *GRIMECH*), as well as for chemical equilibrium. The *GRIMECH* scheme gives the highest abundance for ammonia: 100 times more NH_3 than the nominal model. As a consequence, features of this molecule become noticeable on both the emission and transmission spectra at 1.9, 2.3, 3.0, 4.0, 6.1 and 10.5 μm . The most prominent feature is found at 10.5 μm .

At the moment, our radiative transfer model does not include the contribution of HCN to the opacities. Based on the HCN abundances and associated spectra found by Moses et al. [50], we can expect the spectra to be also sensitive to the HCN abundance. Indeed, at the altitudes probed by the observations, there is nearly 2 orders of magnitude less HCN with our nominal model than with *GRIMECH*, and *GRIMECH* gives HCN abundances similar to that of Moses et al. [50]. Therefore, the signature of HCN found by Moses et al. [50] at 14 μm should also become noticeable with the *GRIMECH* version of our scheme.

Discussion

The modeled abundances of nitrogen-bearing species (in particular NH_3 and HCN) differ significantly depending on the reaction network that we use. Deviations are also found for hydrocarbons in the upper atmosphere. To study the chemical composition of hot atmospheres, we recommend to use, as far as possible, chemical

⁴<http://kurucz.harvard.edu/stars.html>.

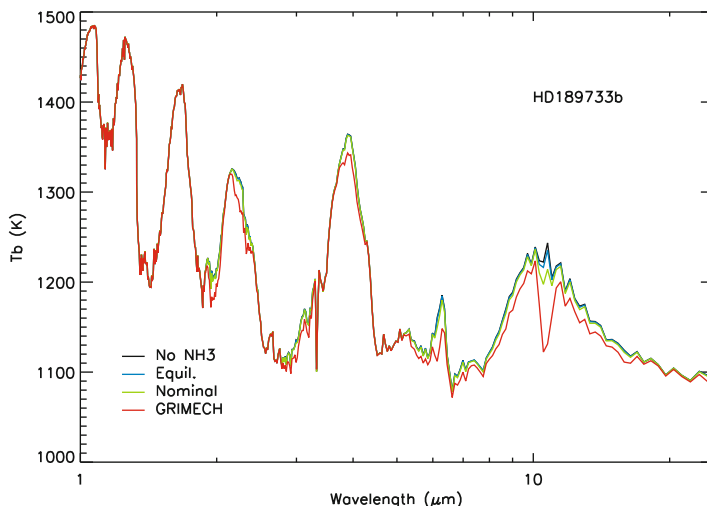


Fig. 6.4 Synthetic day-side spectra of HD 189733b with the nominal mechanism (*green curve*) compared to the one corresponding to the *GRIMECH* mechanism (*red curve*) and to the thermochemical equilibrium (*blue curve*). The *dark curve* is obtained when NH_3 is removed from the model. The day-side fluxes are given as brightness temperatures (T_b). Because of the reflection component, note that the link between T_b and the atmospheric thermal profile is altered below $2\text{ }\mu\text{m}$

schemes validated against experiments, like ours. We do not claim that it is a definite chemical scheme, it will certainly evolve in the same time as our knowledge about nitrogen chemistry. Indeed, kinetics of reactions between nitrogen-bearing species is not as well known as for carbon-bearing species. Nitrogen mechanisms are expected to be improved and completed to study exoplanet atmospheres. For instance, in our chemical scheme we note the absence of several species (such as CH_3CN , HC_3N , ...), which have observable abundances in some planetary atmospheres of the Solar System (Titan and Earth). With solar elemental abundances and in the range of pressures and temperatures that we considered for the planet studied, HCN and NH_3 remain minor species, and it is likely that the departures that we find have little influence on the thermal profile and the spectra of this planet. However, hot Jupiters are certainly significantly enriched in heavy elements if formed by core accretion. A possible signature of that is the high abundance of CO_2 found by observations [64, 65], that requires a high metallicity [73]. In addition, C/O ratios could be altered during planet formation and a high C/O ratio could explain the high observed abundances of both CH_4 and CO_2 [48]. If this is correct, then HCN should be a key species and a main reservoir of both C and N in atmospheric layers probed by observations. New observations able to constrain the abundance of NH_3 and/or HCN would be extremely useful.

Conclusion

Since decades, the field of combustion deals with high temperatures and pressures, similar to the ones found in hot Jupiters. Models used for industrial applications (such as car engine simulations) have been developed and validated over a broad range of temperatures, pressures and compositions. An important work of experiments have been required to obtain such a chemical scheme. We can benefit from this expertise and use the same chemical scheme to study the atmospheric composition of planets with warm atmospheres, as hot Jupiters and hot Neptunes. Despite this hard work, nitrogen chemistry is still not well constrained. Different schemes exist and are commonly used in the combustion field to study different purposes. Using these schemes in a photochemical model give a large range of possible results. This confirms the fact that chemical networks, in particular for N-bearing species, will have to be tested experimentally in conditions that are closer to those prevailing in hot exoplanet atmospheres. These planets represent a real laboratory to study nitrogen chemistry. We can hope that future, more accurate observations obtained for instance with EChO and JWST, will provide constraints allowing us to improve our mechanisms.

Acknowledgements We thank Ignasi Ribas for providing us the UV flux of ϵ Eridani, proxy of HD 189733 and Anthony M. Dean for providing us the list of rate coefficients from his book in an electronic form. F. S., O. V., E. H. and M. A. acknowledge support from the European Research Council (ERC Grant 209622: E₃ARTHs).

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